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COMPOUND SEMICONDUCTOR SURFACES AND INTERFACES(U)  
COLORADO STATE UNIV FORT COLLINS C W WILMSEN 1986  
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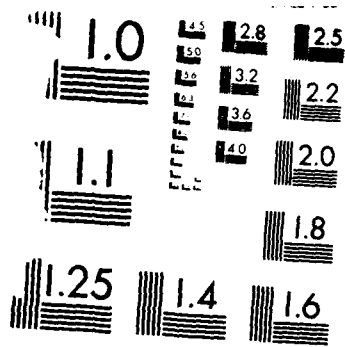
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OFFICE OF NAVAL RESEARCH

FINAL REPORT

for

Contract N00014-76-C-0387

Task No. NR 372-095

Compound Semiconductor Surfaces and Interfaces

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## I. INTRODUCTION

All semiconductor devices and integrated circuits require dielectric layers for interconnect isolation, gate oxides, passivation, etc. Thermally grown  $\text{SiO}_2$  is the primary dielectric film for silicon technology. This ONR contract investigated the chemistry and electrical properties of the interface between III-V compound semiconductors and electrical properties of grown oxides and deposited.

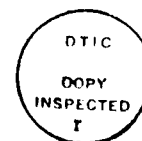
When this study began, very little was known about these oxides or their interfaces. The results of the research supported by this contract has added substantially to the fundamental understanding of the oxide growth, properties and electronic structure. Much of the experimental work was obtained with surface analytical techniques and significant contributions were also made in this field.

The original ONR contract began in October 1975 and initially concentrated on the grown oxides of InP and GaAs. This work evolved over the years to include the study of deposited insulator/InP interfaces and trapping at the interface. The ONR contract has supported the publication of 31 journal articles and book chapters and numerous conference presentations. In addition, there are 5 journal papers presently in preparation. The papers provide considerable detail information covering the research conducted with ONR support. A summary of this information is given in the following section.

## II. Accomplishments of the Contract Research

### A. Deposited insulator/InP interfaces

1. In 1979 we published 2 papers which outlined the probable chemistry of the  $\text{SiO}_2$ /InP interface; this included oxidation of InP, diffusion of In and P into the  $\text{SiO}_2$ , diffusion of Si into the InP, evaporation of the InP surface and chemical reactions between the  $\text{SiO}_2$  and the InP.
2. As part of 1 above, we used Auger profiles to show that even at a



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deposition temperature of  $340^{\circ}\text{C}$ , In will diffuse into the  $\text{SiO}_2$ . As will be discussed later, this In is oxidized and may contribute to the interface traps observed on InP.

3. Also as part of 1 above we predicted that the  $\text{SiO}_2$  deposition could increase the N type doping of the InP surface and hence cause type inversion of P type substrates. There is now some evidence to support this prediction.
4. The thermodynamics of possible Si, SiO,  $\text{SiO}_2$  reactions with InP and its oxides were worked out and published.
5. The chemical composition of the plasma enhanced and pyrolytically deposited  $\text{SiO}_2$ /InP interface was determined for various in situ and precleaning procedures. It was shown that a native oxide always existed at the interface. This oxide was primarily grown in the deposition chamber and probably could not be avoided by present deposition techniques.
6. By using UPS and ELS techniques the band gap of the thin native oxide of InP ( $\text{InPO}_4$ ) was measured to be 4.5 eV. The band gap of  $\text{InPO}_4$  was not known before these measurements.
7. Using 6 above, the band diagram for thin oxides on InP was determined. This is important for modeling of MIS devices. The diagram showed that  $\text{In}_2\text{O}_3$  mixed with  $\text{InPO}_4$  created a state that could be the cause of the interface trap.
8. A possible relationship between interfacial trap density and insulator deposition was proposed from a careful survey of the literature and the results of 2 and 7 above. This study suggests that the  $\text{In}_2\text{O}_3$  near the interface, as a result of either oxidation or In diffusion, contributes to the trap density.

9. We have directly measured the loss of inversion layer electrons as a function of time using gated Hall devices. Prior to this measurement, the change in drain current was used as a measure of electron trapping. However, this type of measurement assumes a constant electron mobility with inversion density which is not strictly correct.
10. In conjunction with O. Krivanek and S. Liliental the thermal oxide/InP and  $\text{SiO}_2/\text{InP}$  was investigated with high resolution TEM. This work revealed the great variability in the surface roughness resulting from different etches. The layering of the thermal oxide was also clearly observed as was previously shown with XPS profiles.

B. Native oxides of InP

1. The growth rate, chemical composition and interface properties of thermal, anodic, plasma, air, laser enhanced and chemically grown oxides of InP have been investigated.
2. We were the first to report XPS profiles of native oxides of InP and to demonstrate the usefulness of the XPS profiling technique on III-V oxides.
3. We were the first to report on the properties of thermal, anodic and laser enhanced oxides growth on InP.
4. The thermal oxidation of InP was shown to begin with a layer of  $\text{InPO}_4$ . The subsequent layers, however, were found to contain increasing concentrations of  $\text{In}_2\text{O}_3$ . This was determined to be caused by the slow diffusion of P through the  $\text{InPO}_4$  which resulted in a buildup of elemental P at the interface. The formation of  $\text{In}_2\text{O}_3$  in the outer layer relates to the interface traps as described in section II.A.8.
5. Our contributions to the understanding of InP anodic oxidation are

significant beginning with the 1975 PCSI-2 paper which demonstrated that the surface potential of InP could be varied and that inversion of the surface was possible. We have also shown that oxidation is initiated by the island growth process, that the interface has uniform composition and that annealing can convert the grown oxide into  $\text{InPO}_4$ . The later requires high temperatures and this causes considerable roughening of the surface.

6. The rate of oxide growth in air was shown to be strongly dependent upon the humidity. This is important for mass production processes of InP integrated circuits since the surface of these circuits usually requires exposure to air. These thin layers were found to be  $\text{InPO}_4$  and relatively stable for  $T < 550^\circ\text{C}$ . In high vacuum the thin air grown oxide act as a protective skin up to  $550^\circ\text{C}$ . Above this temperature the vapor pressure of the substrate cause the oxide to rupture and the InP surface to rapidly evaporate.
7. The surface of InP exposed to  $\text{N}_2\text{O}$  does not grow a significant thickness of oxide, even when the temperature reaches  $400^\circ\text{C}$ . With strong light present, such as a laser of proper wave length, the oxide grows rapidly with a strong dependence upon laser intensity, substrate temperature and  $\text{N}_2\text{O}$  pressure. The parameter variation provides interesting kinetic information as well as guidelines for laser assisted deposition of  $\text{SiO}_2$ .
8. The growth of a plasma oxide on InP was found to be independent of substrate temperature below  $350^\circ\text{C}$  but to be strongly dependent upon the proximity of the substrate to the plasma.
9. Chemically grown oxides, i.e., ones grown in  $\text{HNO}_3$  or  $\text{H}_2\text{O}_2$  are strongly correlated with the InP conductivity type and doping, incident light

and bath temperature. Thousands of Angstroms of oxide can be grown on N type in a few minutes where as only 20-40 Å can be grown on P type. The oxide is composed of  $\text{InPO}_4$  and no  $\text{P}_2\text{O}_5$  and  $\text{In}_2\text{O}_3$  as is the case with anodic oxides.

C. Anodic oxides of GaAs

1. The GaAs/anodic oxide interface was extensively investigated. Our measurements indicated that a thin  $\text{Ga}_2\text{O}_3$  inner layer exists at the interface. This was later reported by others although the Bell Labs group believe otherwise. Some recent high resolution TEM studies by Ondrej Krivanek at Arizona State University to verify our conclusion.
2. In relation to 1 above, we showed that the  $\text{Ga}_2\text{O}_3$  began with the initial island growth. Once established, the interfacial layer remained unchanged with oxide growth.

D. The sputtered Si surface

1. UPS studies of the sputtered Si surface were conducted and resulted in a model for the damaged Si layer. This was accomplished by utilizing the difference in the mean escape depth of the HeI and HeII spectra. The data indicates that the outer 4-5 Å had many broken bonds, the next 10 Å had few broken bonds, but considerable dilation of the bond angles from implanted sputter gas atoms was found below these layers.
2. Exposure of this sputtered surface to oxygen resulted in a rapid uptake of oxygen by the outer layer, mostly as an oxide layer. The inner layer absorbed oxygen but much more slowly.



### III. Refereed publications with support from the contract

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3. MOS Processing for III-V Compound Semiconductors: Overview and Bibliography, C. W. Wilmsen and S. Szpak, Thin Solid Films, 46 (1977) 17-45.
4. Single and Double Layer Insulator MOS Capacitors on InAs, C. W. Wilmsen, L. G. Meiners, and D. A. Collins, Thin Solid Films, 46 (1977) 331-337.
5. Improvement of Grown Oxides for Surface Protection, C. W. Wilmsen and R. W. Kee, Thin Solid Films, 51, 93 (1978).
6. Analysis of the Oxide/Semiconductor Interface using Auger and ESCA as Applied to InP and GaAs, C. W. Wilmsen and R. W. Kee, J. Vac. Sci. Technol., 15, 1513 (1978).
7. Interface Characteristics of Thermal SiO<sub>2</sub> on SiC, R. W. Kee, K. M. Geib, C. W. Wilmsen, and D. K. Ferry, J. Vac. Sci. Technol., 15, 1520 (1978).
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10. Deposited Insulator Layer/GaAs and InP Interface Formation, C. W. Wilmsen, R. W. Kee, J. F. Wager, J. Stannard and L. Messick, Thin Solid Films, 64, 49 (1979).

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17. Oxygen Adsorption on the Disordered Silicon Surface, D. L. Ellsworth and C. W. Wilmsen, J. Vac. Sci. Technol. 19, 513 (1981).
18. The Chemical Composition and Formation of Thermal and Anodic Oxides/III-V Compound Semiconductor Interfaces, A Critical Review, C. W. Wilmsen, J. Vac. Sci. Technol., 19, 279 (1981).
19. The Plasma-Enhanced Chemical Vapor Deposited  $\text{SiO}_2/\text{InP}$  Interface, J. F. Wager and C. W. Wilmsen, J. Appl. Phys. 53, 5789 (1982).
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23. Traps at the Deposited Insulator/InP Interface - A Discussion of a Possible Cause, C. W. Wilmsen, J. F. Wager, K. M. Geib, T. Hwang and M. Fathipour, Thin Solid Films, 103, 47 (1983).
24. Photo enhanced thermal oxidation of InP, M. Fathipour, K. Boyer, G. J. Collins, C. W. Wilmsen, J. Appl. Phys., 57, 637 (1985).
25. New Model for slow drift in InP metal-insulator-semiconductor - field effect transistors, S. M. Goodnick, T. H. Wang and C. W. Wilmsen, Appl. Phys. Lett., 44, 453, (1984).
26. Influence of interfacial structures on the electronic properties of SiO<sub>2</sub>/InP MISFETs, K. M. Geib, S. M. Goodnick, D. Y. Lin, R. G. Gann, C. W. Wilmsen and J. F. Wager, J. Vac. Sci. Technol. B2, 516 (1984).
27. Insulator/Semiconductor Interfaces, C. W. Wilmsen in The Physics of Submicron Devices edited by H. L. Grubin, Plenum Press.
28. Oxide/Semiconductor Interfaces, C. W. Wilmsen, in The Physics and Chemistry of III-V Semiconductor Interfaces edited by C. W. Wilmsen, Plenum Press.
29. Deposited Insulator/III-V Interface, J. F. Wager and C. W. Wilmsen in The Physics and Chemistry of III-V Semiconductor Interfaces edited by C. W. Wilmsen, Plenum Press.
30. A Combined HREM , XPS and Electrical Properties Study of the InP-SiO<sub>2</sub> Interface, O. L. Krivanek, Z. Liliental, J. F. Wager, R. G. Gann, S. M. Goodnick and C. W. Wilmsen. J. Vac. Sci. Technol. to be published.
31. HREM Investigation of the InP-SiO<sub>2</sub> Interface, Z. Liliental, O. L. Krivanek, J. F. Wager and S. M. Goodnick, Appl. Phys. Lett. to be published.

IV. Personnel Supported by the Contract

C. W. Wilmsen - Principal Investigator  
S. M. Goodnick - Research Associate/Post Doc.  
K. M. Geib - Research Associate (Awarded an M. S. degree)  
R. W. Kee - Awarded an M.S. degree  
J. F. Wager - Awarded the Ph.D. degree  
D. L. Ellsworth - Awarded the Ph.D. degree  
M. Fathipour - Awarded the M.S. and Ph.D. degrees  
T. Hwang - Ph.D. to be awarded (Spring 85)  
Summary 3 M.S. and 4 Ph.D. degrees awarded.

END

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